

VOLATILIZATION IN A VACUUM OF ELEMENTS FROM
MELTS OF PLANETARY SURFACE MATERIAL

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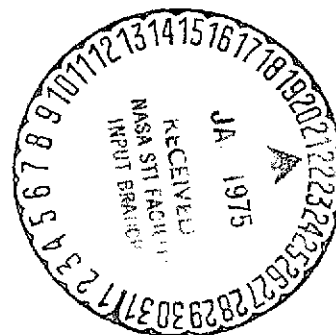
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ANNOTATION

Endogenic and exogenic events leading to the appearance of large volumes of molten material on the lunar surface must be accompanied by volatilization of elements in the vacuum [1]. However, until recently, it has not been clear whether the process of volatilization actually occurs on the Moon. This would explain the lowering (compared to the Earth) of the content of certain elements on the lunar surface (Na, K, etc.). In the literature on this topic, there are contradictory conclusions (O'Hara, Ringvud, and others) [2]. The many laboratory experiments on similar processes [3 - 15] are not sufficient for an interpretation, primarily due to the absence of an adequate physical model and theory of the process, and also because of the limited range of parameters (T , p , τ) accessible in the various experimental methods.

In the present work, a physical model is worked out and a theory is presented on the basis of an analysis of the experimental data for the process of vaporization of volatile components of molten rock in vacuum, taking into account the adsorption of gases from the residual atmosphere. This model and theory then allow us to interpret such processes. As a result, several preliminary conclusions are presented relative to such phenomena on the Moon and their laboratory modeling.

VOLATILIZATION IN A VACUUM OF ELEMENTS FROM MELTS OF PLANETARY SURFACE MATERIAL

M. D. Nusinov and Yu. B. Chernyak

1. A Basic Physical Introduction to the Process of Volatilization

From the standpoint of thermodynamics, a system in which a constant temperature is maintained and which is continuously evacuated is a typical nonequilibrium (open) system, in which a state of equilibrium never exists.

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Studying the behavior of a melt of composite composition under such circumstances, it is found that the process of its vaporization will proceed monotonically all the way to full vaporization of the melt. Various components of the melt will exhibit different characteristic times of vaporization. These times may differ from each other by many orders of magnitude. From this, it is clear that if, during the vaporization of any element, the speed of the process sharply drops and the concentration practically stabilizes, then it must be that the given element either has undergone a chemical reaction to a compound with significantly

*Numbers in the margin indicate pagination in the original foreign text.

lower volatility, or that the element was in that state to begin with.

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Indeed, this is indicated by mass spectrometric studies of the composition of the vapors above molten rock in a vacuum, which showed [13, 14] that most of the volatile alkali metals reside in the atomic state. This shows that before leaving the melt, the molecule resides in a dissolved state in the melt, in which it experiences the weakest binding to the basic material. As has already been mentioned, a volatile element may enter into a compound with significantly lower volatility (e.g., Na_2O , H_2O , etc.), and thus be firmly bound chemically to the matrix of the basic material.

The binding energy of an element with the melt is characterized by the enthalpy (heat) of the transition. In accordance with this, the speed of vaporization of an element residing in various compounds will differ greatly, due to the exponential temperature factor. This allows us, from a kinetic standpoint, to consider elements only in two states: a volatile dissolved state (with the least binding energy to the melt), and non-volatile.

Chemical changes (oxidation, for example) may be caused by the presence of an adsorbed layer on the surface of the melt, from the residual gases, which leads to a dependence of the component concentrations on pressure. On the other hand, the same layer ("contamination") may, in a low vacuum, decidedly reduce the speed of vaporization, as has already been shown by Knudson [16]. This also leads to a dependence on pressure [17, 18].

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It is important to emphasize that the analysis of the experimental dependence on time, pressure, and temperature provides the key to the construction of a physical model for the process. Therefore, we shall now present an overview of the experimental data.

2. Brief Summary of the Experimental Data

The kinetics of the process of sodium and potassium vaporization from molten rock (including lunar material) are presented in Figures 1 and 2 [6, 7, 8, 13].

All of these curves are characterized by the presence of a region of rapid, exponential decrease in concentration of the component during the time (α), which will be called the kinetic stage. The second period is "quasi-stationary", that is, with practically constant concentration (δ). For the latter, the characteristic time of vaporization is an order of magnitude longer than for the first. The reader's attention is called to the two-stage character of the K concentration variation in the low temperature (1150 - 1175° C) experiments of O'Hara [6,7] (Figure 2b), the nature of which will be explained below.

Investigations into the dependence on pressure of the vaporization in vacuum of the base elements (Si, Al, Fe, Mg, Ca, Na, K) have been carried out at the Institute for Space Research of the Academy of Sciences USSR [IKI] [12], on two types of basalt in the region of "quasi-stationary" behavior. Typical results for the most volatile elements, Na and K, are presented in Figures 3 and 4. Determination of the chemical composition of the residual material was carried out by two independent processes, micro-x-ray spectroscopy and chemical analysis. Both methods gave similar results. Down to a certain characteristic pressure (P_0), the concentration does not change. As the pressure is decreased further, a decrease in the concentration is observed according to a power law with a characteristic power $\gamma \sim 10^{-1}$ (Na and K) and $\gamma \sim 10^{-2}$ for the remaining elements. The exponent γ is observed to increase with temperature. A similar pressure dependence is characteristic of adsorption processes [19, 20]. In Figure 5 and 6, the temperature dependence of the vaporization of the base elements in vacuum from molten rock, minerals, and also lunar material is presented [6 - 13]. Attention is

called to the presence of a characteristic temperature T_0 and the heat of the process ψ , determined by the slope of the dependence in the region $T > T_0$. Below, it will be shown that the existence of two regions of pressure ($P \gtrless P_0$) and two regions of temperature ($T \gtrless T_0$) is determined by the relation between the speed of vaporization of the element and its conversion into non-volatile material.

3. Elements of the Theory of Vaporization of a Multi-Component Solution in a Vacuum in the Presence of Chemical Reactions

As has been shown in [21], the vaporization of volatile components from a melt is observed as vaporization of dissolved elements. The kinetics of vaporization from a multi-component mixture in our case may be reduced to the same question for a two-component system for the following reasons: In the first place, the speeds of vaporization for different elements are usually so different that one may consider the vaporization of each in turn, independent in time from the vaporization of others. Second, even in the event that two elements have similar vaporization rates (for instance, Na and K), then, due to the small concentration of each, it will not cause a noticeable effect. /7

Let us define X_1 and X_2 to be the volume concentration of a melt element (per cm^3) in the volatile and nonvolatile states, respectively. Then the total concentration X of the element will be given by:

$$X = X_1 + X_2. \quad (1)$$

We shall assume that:

1) the time of the process T_f is not too large, that is, so that the vaporization of the remaining material (the "solvent") may be disregarded;

(2) the process takes place in such a small volume that the element transport time to the surface $\tau_{tr} \ll \tau_f$. Then the kinetic equation for the concentrations X_1 and X_2 may be written in the form:

$$\frac{dX_1}{dt} = -j_f + j_b + K_{21}X_2 - K_{12}X_1, \quad (2)$$

$$\frac{dX_2}{dt} = -K_{21}X_2 + K_{12}X_1. \quad (3)$$

The mass transfer to the surrounding vacuum environment may be written as the difference between the forward and backward flows $j_f + j_b$, and the conversion between the volatile and nonvolatile states /8 of the element may be written:

$$K_{21}X_2 - K_{12}X_1.$$

A detailed analysis of the mechanism by which a molecule returns to the melt shows that the reverse current (j_b) is proportional to the forward current (j_f) [22, 23],

$$j_b = Z(p) \cdot j_f \quad (4)$$

and, in the pressure range $Z \ll 1$ of interest to us, the coefficient of return Z is small,

$$Z \ll 1. \quad (5)$$

Thus:

$$-j_f + j_b = -j_f(1 - Z). \quad (6)$$

The current of evaporating particles j_f from the surface S of the melt having a volume V , is usually related to the saturation vapor pressure $P_1(T)$ above the mixture [17]:

$$j_f = \frac{1}{h} \alpha_v \frac{P_1(T)}{\sqrt{2\pi m k T}}; \quad h = \frac{V}{S}. \quad (7)$$

Here, α_v is the vaporization coefficient [18]; h is a characteristic depth of the molten rock, m is the mass of the evaporating molecules or atoms, k is the Boltzmann constant.

Let us now denote the mole fraction of the volatile component in the solution as \bar{X}_1 . Since $X_1 \ll 1$, it is a sufficient approximation to consider the solution regular, with a heat of mixing equal to $\Delta H \cdot A \cdot \bar{X}_1 (1 - \bar{X}_1)$, ($A = \text{const}$) [21, 24]. The pressure $P_1(T)$ is then given by:

$$P_1(T) = \bar{P}_1(T) \cdot \bar{X}_1 \cdot e^{\frac{A(1-\bar{X}_1)^2}{RT}}, \quad (8)$$

where $\bar{P}_1(T)$ is the vapor pressure of the evaporating material in the pure state at the same temperature. A is the universal gas constant. We note that the larger A is (in the algebraic sense), the more rapid is the vaporization of the component ($\Delta H_m \sim 10 + 20 \frac{\text{k cal}}{\text{mole}}$) [24, 25]. In the case of interest to us $\bar{X}_1 \ll 1$, so $\bar{X}_1 = \frac{\mu}{\rho} \cdot X_1$. (μ and ρ are the molecular weight and density of the solvent, respectively) and $(1 - \bar{X}_1)^2 \approx 1 - 2\bar{X}_1$. It follows that:

$$P_1(T) = e^{\frac{A}{RT} \cdot \frac{\mu}{\rho}} \cdot \bar{P}_1(T) \cdot X_1 \cdot e^{-\frac{2A\mu}{RT\rho} X_1} \quad (9)$$

Denoting the multiplier of X_1 in the exponent as β , and the product

$$(1 - \beta) \cdot \frac{\Delta v}{h} (2\pi mkT)^{-\frac{1}{2}} \cdot e^{\frac{A}{RT} \cdot \frac{\mu}{\rho}} \cdot \bar{P}_1(T) = j_1(T, \beta) \quad (10)$$

finally, we obtain:

$$j_1 - j_2 = -j_1 \cdot X_1 \cdot e^{-\beta X_1}; \quad \beta = \frac{2A\mu}{RT\rho} \quad (11)$$

In order to clarify the relationship between j_1 , K_{21} , and K_{12} , we compare the solution of Equations (2) and (3) for long times with the experimental curves in Figures 1 and 2. As $t \rightarrow \infty$, the concentration X_1 is sufficiently small ($\beta X_1 \ll 1$) and the equations may be linearized:

$$\frac{dX_1}{dt} = -(j_1 + K_{12})X_1 + K_{21} \cdot X_2, \quad (12)$$

$$\frac{dX_2}{dt} = -K_{21} \cdot X_2 + K_{12} \cdot X_1. \quad (13)$$

The general solution of such a system of equations has the form:

$$\begin{aligned} x_1 &= \sum a_{ij} \cdot e^{-\lambda_{ij} t}, \quad i, j = 1, 2; \quad a_{ij} = \text{const.} \\ \lambda_{12} &= \frac{K_{12} + K_{21} + J_1}{2} \pm \sqrt{\left(\frac{K_{12} + K_{21} + J_1}{2}\right)^2 - J_1 \cdot K_{21}} \end{aligned} \quad (14)$$

The presence of the "quasi-stationary" region in Figures 1 and 2 shows that:

$$\lambda_2 \ll \lambda_1, \quad (15)$$

from which we may conclude that:

$$K_{21} \ll J_1 + K_{12}. \quad (16)$$

This shows that in the observed experimental processes, the conversion of the element from the nonvolatile state is, for practical purposes, absent. On the other hand, except for the dependence on (15), the relationship between the initial and final concentrations X_0 and X_∞

$$X_0 \gg X_\infty, \quad (17)$$

which is usually satisfied, allows one to write:

$$X_0 \approx X_{10} \gg X_{20}; \quad (X_{10} + X_{20} = X_0), \quad (18)$$

where X_{10} and X_{20} are the initial concentrations of the element in the volatile and nonvolatile states. /10

The Inequality (18) implies that the large majority of the molecules reside in the volatile state initially. On the contrary, if $X_0 \sim X_\infty$, then in the initial composition the majority of the molecules are nonvolatile.

The Inequality (16), reinforcing the Inequality (18), allows us to discard the term $K_{21} \cdot X_2$ in the system of nonlinear equations (2), (3), which then take the form:

$$\frac{dx_1}{dt} = -J_1 \cdot x_1 \cdot e^{-P x_1} - K_{12} \cdot x_1, \quad (19)$$

$$\frac{dx_2}{dt} = K_{12} \cdot x_1. \quad (20)$$

The system (19), (20) is easily solved by quadrature:

$$\int_{x_{10}}^{x_1(t)} \frac{dx}{x_1 e^{-\beta x} + \frac{K_{12}}{J_1}} = - \int_0^t dt, \quad (21)$$

$$X_2(t) = X_{20} + K_{12} \int_0^t X_1(t) \cdot dt. \quad (22)$$

From Equation (21), one may see that X_1 decreases to zero monotonically with time, while Equation (22) leads to a monotonic growth of $X_2(t)$. Indeed, the difference $X_2(t) - X_{20}$ is proportional to the area under the integrand $X_1(t)$.

Let us consider the qualitative behavior of $X_1(t)$, which does not change if we remove the term K_{12}/J_1 from Equation (21). We then obtain

$$E_i^*(\beta x_1) - E_i^*(\beta x_{10}) = - \int_0^t dt, \quad (23)$$

where $E_i^*(Z)$ is the tabulated exponential integral [26]:

$$E_i^*(z) = \int_z^\infty \frac{e^{-u}}{u} \cdot du. \quad (24)$$

Equation (23) gives the universal dependence of the dimensionless concentration $\mathcal{U} = \beta X_1(t)$ as a function of the dimensionless time $\mathcal{T} = \int_0^t dt$. It is clear that different initial concentrations $\mathcal{U}_0 = \beta x_{10}$ correspond to displacement of the initial time by the quantity $|E_i^*(\beta x_{10})|$ in the universal relation Equation (23). /11

In Figure 7, the universal curve $\mathcal{U}(\mathcal{T})$, along with $X_2(t)$ of the total concentration $X(t) = X_1(t) + X_2(t)$, are presented for two initial concentrations x'_{10}, x''_{10} . From the figure, it is evident that it is possible to have two types of kinetic behavior in the form of two- and one-stage curves. The first of these is realized when:

$$\frac{2A\gamma}{RTS} \cdot x_{10} \approx \mathcal{U}_0 \approx 5, \quad (25)$$

And the second, the one-stage behavior, is realized in the opposite case. In particular, if $\frac{2A\gamma}{RTS} x_{10} \ll 1$, then the decrease of $X(t)$

immediately begins [from the region of exponential decrease in $X_1(t)$]. All the above-mentioned cases are observed in Figures 1 and 2.

We now proceed to the analysis of the dependence of concentration on pressure, obtained in the "quasi-stationary" mode at long times ($\tau_f \sim 1$ hr). The time dependence correlates with the condition $U_0 < 1$, for which in (21) the equations $(e^{-\rho x})$ and

$$X_2(t) = X_{10} \cdot e^{-(j_1 + K_{12})t} \quad (26)$$

are linearized. Since $X_1(\infty) = 0$, it follows that:

$$X(\infty) = X_2(\infty) = X_{20} + \int_0^\infty X_{10} \cdot e^{-(j_1 + K_{12})t} \cdot dt \quad (27)$$

From this we obtain:

$$X_{\infty} = X_{20} + X_{10} \frac{K_{12}}{j_1 + K_{12}} \quad (28)$$

Expression (28) with $X_{20} = \text{const} \neq 0$ cannot yield the observed power law pressure dependence of X_{∞} . Therefore, we assume that $X_{20} = 0$, [compare with (18)], and then we have: we have: /12

$$X_{\infty} = \frac{K_{12} \cdot X_{10}}{j_1 + K_{12}} \quad (29)$$

On the other hand, the dependence of j_1 on pressure, according to (10), is determined by the factor:

$$j_1 \sim \alpha_v(\rho) \cdot [1 - Z(\rho)], \quad (30)$$

which in the case of high vacuum approaches a value of unity $(\alpha_v \rightarrow 1, Z \rightarrow 0)$ [17, 18, 22, 23]. It is easy to see that the observed pressure dependence may be obtained only if $j_1 \gg K_{12} (\rho < \rho_0)$. In fact, if the opposite condition is satisfied, K_{12} cancels from Equation (29), and X_{∞} ceases to depend on pressure, as is observed for $p > p_0$:

$$j_1 \ll K_{12} \quad (\rho > \rho_0)$$

The pressure P_0 is determined by the condition:

$$f_1(P_0) = K_{12}(P_0). \quad (31)$$

Thus, in the case of high vacuum,

$$K_{12} \sim p^\gamma \quad \text{where } \gamma = \text{const.}$$

Such a pressure dependence is characteristic of the Freundlich adsorption isotherm [19, 20]:

$$n(p) = n_0 \cdot p^\gamma \cdot e^{\frac{q}{RT}}, \quad (32)$$

here $n(p)$ is the concentration of the adsorbed molecules (atoms) in the residual atmosphere, and q_v is the heat of adsorption (~ 1 kcal/mole) [19, 20].

It is natural to assume that:

$$K_{12} \sim n(p). \quad (33)$$

This further confirms the character of the temperature dependence of γ on T , which is the same as that of the adsorption isotherm. /13

The molecular mechanism for the dependence of K_{12} on p (and on T) is apparently the following: oxygen, adsorbed on the surface of the melt from the background gas, oxidizes a portion of the departing atoms (molecules) of the volatile component, converting them to a nonvolatile compound. Such a reaction is typically binary, hence,

$$K_{12} = n(p) \cdot e^{\frac{-Q}{RT}} \cdot \text{const.}, \quad (34)$$

where Q is the activation energy for the given reaction (~ 1 kcal/mole [27]). It is interesting to note that such a mechanism requires the presence of a diffusion current of oxidized molecules, directed into the melt.

Let us now consider the temperature dependence of $X_\infty(T)$. From Equations (32) and (34), we obtain:

$$K_{12} = a e^{-\frac{Q-Q_v}{RT}} \quad \text{where } a = \text{const.} \quad (35)$$

Proceeding in analogy with Equation (10), we find:

$$j_1 = b \cdot e^{-\frac{L-A}{RT}}; \quad b = \text{const.}, \quad (36)$$

where L is the latent heat of volatilization for the pure component (for Na, L=25 kcal/mole [28]). Using Equations (35) and (36) from (29), we obtain:

$$\text{and } x_{\infty} = x_0 \frac{a e^{-\frac{Q-Q_v}{RT}}}{b e^{-\frac{L-A}{RT}} + a e^{-\frac{Q-Q_v}{RT}}}, \quad (37)$$

$$(38)$$

The observed exponential temperature dependence shown in Figure 5 (for $T > T_0$) can agree with Equation (37) only in the event that the second term (K_{12}) in the denominator of Equation (37) is much smaller than the first (j_1). In the opposite case, for $T < T_0$, we have $j_1 \ll K_{12}$.

These two regions of temperature arise if:

$$L - A > Q - Q_v$$

which is always true. The temperature T_0 thus has a simple physical meaning: for $T < T_0$, the predominant process is the chemical reaction $[X_1 \rightarrow X_2]$ ($x_{\infty} \approx x_0 \approx x_o$). For $T > T_0$, the process of volatilization dominates ($x_{\infty} \approx \frac{K_{12}}{j_1} x_o \ll x_o$). It is clear that the temperature T_0 is determined by a condition analogous to Equation (31):

$$j(T_0) = K_{12}(T_0), \quad (39)$$

from which:

$$T_0 = \frac{1}{R} \left(\frac{L - A - Q + Q_v}{\ln \frac{b}{a}} \right). \quad (40)$$

So, the assumptions developed here allow us to explain qualitatively all the observed peculiarities of the experimental dependence of x_{∞}

on τ_f , p , and T in the region of low pressures and moderate temperatures.

At temperatures higher than the dissociation temperature for alkali metal oxides, the coefficient K_{21} will be different from zero, and the kinetics of the vaporization process will be modified.

At sufficiently high pressures $P \gg p_0$, the thickness of the adsorbed layer will stabilize and, therefore, K_{12} and α_v will cease to depend on pressure. However, in this region $Z(p) \sim 1$ and depends strongly on pressure. As a consequence, the kinetics of the process and their pressure dependence are both modified.

4. Characteristics of Volatilization on the Moon

Let us now consider how much we may use the results obtained toward understanding the processes of volatilization on the Moon (and also on other celestial bodies lacking atmospheres) from melts resulting from endogenic (volcanic) events. We shall show that under real lunar conditions, over a wide range of temperatures, the kinetic type of volatilization is realized. From Equations (32) - (34) it follows that, in the high vacuum of the moon, $K_{12} = 0^*$, and the residual concentration $X_\infty \rightarrow 0$ after sufficiently long volatilization times. /15

On the other hand, an estimate of the value of X_0 from Equation (25) using the parameters of lunar material, obtained from Figure 5 [8], shows that for temperatures in the range 250 - 300° K, the kinetic type of volatilization of Na and K occurs when the initial concentration $X_0 \leq 5\%$. It follows that under lunar conditions only the rapid exponential mode of vaporization is realized:

*The fact that when lunar material is heated [8] (Figure 1) there is a kinetic mode of vaporization attests to the practical absence of oxygen in the lunar atmosphere at the time when the material was molten.

$$x_{\infty} = x_0 \cdot e^{-j_0 \cdot t} \quad (36)$$

The observed concentration of Na and K in lunar material is determined by the fact that in the corresponding temperature regime, the process had not proceeded to completion. In the treatment of the preceding theoretical section, it was assumed that the processes of transport of the volatile material to the surface are not limiting, that is, the volatilization takes place from a sufficiently thin layer (of thickness h). In laboratory experiments, h was equal to the full depth of the melt, as is characteristic for vaporization from liquid phases as a result of evaporation with a convective-diffusive transport mechanism.

Under real conditions, the thickness of this layer will be strongly dependent on the ratios of the volatilization and transport rates. It is clear that this layer will be thinnest in the case of volatilization from the solid phase as a result of the sublimation, and purely diffusional transport. For diffusional transport, the time constant of such a process is given by:

$$\tau_d \approx \frac{h^2}{D} \quad (37)$$

where D is the diffusion coefficient.

Denoting the multiplier of $1/h$ in Equation (10) as j_0 , we obtain $j_1 = j_0 \cdot \frac{1}{h}$. Equating τ_d with the time constant for volatilization $\tau_j = \frac{1}{j_1}$, we obtain an expression for the thickness of the layer of lunar material depleted of the volatile components:

$$h = \sqrt{D \cdot j_0} \quad (38)$$

Since $D = D_0 \cdot e^{-\Delta E / RT}$, (ΔE is the activation energy for diffusion) and $j_0 \sim e^{-\frac{4-A}{RT}}$, it follows that h is very strongly temperature dependent:

$$h \sim e^{-\frac{h + \Delta E - A}{3RT}} \quad (39)$$

Due to the large values of ΔE ($1.0 - 10^2$ kcal/mole) [27], the depth h thus established depends very strongly on the entire thermal history of the layer. Nevertheless, we must stress that the kinetic character and high speed of the volatilization process without question demonstrates that such processes proceed with greater intensity on the Moon. In Table 1, we present the time constant for volatilization /17 $\tau_g = \frac{f}{f_0}$ for lunar material with $h \sim 1$ cm at various temperatures.

TABLE 1.

$T, ^\circ K$	1500° K	900° K	500° K	300° K
τ_g	0.65 days*	5 days*	25 days*	300 years

* Earth days.

Hence, the depletion of the surface layer of the moon of Na and K constitutes convincing proof that processes of volatilization have taken place [25].

Elements volatilizing from lunar material will be removed from the lunar atmosphere as a result of multiple cyclical processes of exogenic origin [emission and sputtering by the charged particles of the "solar wind" (electrodesorption, etc.), photodesorption by solar photons, micrometeorite bombardment, etc.]. If these processes took on a global character, they would have contributed to the chemical bonding of the residual oxygen and its removal from the lunar atmosphere.

5. On the Question of Laboratory Modeling of Volatilization Processes

The often stated requirement of the necessity of accurate reproduction of lunar vacuum conditions ($p \sim 10^{-10} - 10^{-12}$ torr) is, in most cases, an unjustifiably rigid condition for the following reason: For the study of the kinetics of volatilization, the pressure maintained in the vacuum apparatus must be such that the

process of volatilization occurs necessarily in the kinetic regime ($j_1 \gg K_{12}$). That is, it is necessary that

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$$p \ll p_0 \quad (40)$$

This condition assures as well the fulfillment of the conditions $\alpha_v \rightarrow 1$ and $Z \rightarrow 0$. In practice, however, it is sufficient to obtain the pressure within two or three orders of magnitude. For volatile elements with γ in Equation (32) $\sim 10^{-2}$, this condition may be weakened to simply $p \lesssim p_0$.

Another method, which allows one to prevent the occurrence of oxidation processes, is (instead of lowering p) to replace the background with an inert gas. The pressure simulated in this case is determined by $Z \ll 1$. However, there is one simulation problem, requiring the reproduction in the laboratory of ultra-high vacuum, close to that of the moon ($p \sim 10^{-10} - 10^{-12}$ torr). This problem is the accurate determination of the partial pressure of oxygen which was present in the lunar atmosphere at the moment of hardening of the material. Such an experiment is extremely interesting, regardless of the large technical difficulties (requiring very large pumping speed of the laboratory apparatus, as high as $10^5 - 10^7$ l/sec).

The choice of experimental temperature also represents an important problem in simulation. When studying the process of volatilization from a thin surface layer, it is necessary to satisfy the condition $T > T_0$. In the study of transport processes, it is necessary to study the behavior of the process over a wide range of temperature ($T \lesssim T_0$)

In conclusion, we point out that as the experimental basis for the presentation given here, we have used results on the pressure dependence $p \sim \sqrt{v_2}$, which, to the knowledge of the present authors, is not covered in the literature, with the exception of [12].

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6. On the Role of Meteorite Bombardment in the Volatilization Process

It is usually said, with one minor exception [29], that volatilization of elements takes place from melts formed by meteoric impact. We shall now discuss the difference between the processes of evaporation and volatilization of elements from the liquid phase.

During a meteoric impact, a rather small amount of material from the target will be evaporated at a very high temperature ($\sim 10^4 - 10^6$ K), during which all the material will escape. A different portion of the material of the target will be melted. This liquid is either formed into very small droplets (to 1 micron) or smeared into a thin layer on the crater wall.

In this case, as will be shown below, the time constant of solidification τ_s is significantly smaller than the time constant of volatilization τ_f . To begin, we shall carry out an estimate verifying that the accumulations of liquid mass (lakes, "puddles", etc.) do not occur in a meteor impact. The speed of movement u of the medium behind the shock waves is connected with the specific energy ϵ in the same region by the relationship $\epsilon \sim u^2/2$. Melting will take place if the condition $\epsilon \gg \epsilon_m$ is fulfilled. It follows that $u \gg \sqrt{2\epsilon_m}$. If $\epsilon_m \sim 5 \cdot 10^9$ erg/gm [30], we have,

$$u \sim 10^5 \text{ m/sec.}$$

Therefore, the liquid will be thrown out of the crater at a high velocity. Only at the point of contact between the liquid and the crater wall (that is, in the hydrodynamic boundary layer) will the speed of movement of the flowing vitreous mass be low enough to allow the formation of a glassy layer.

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We shall investigate the possibility of forming a boundary layer of flowing liquid in the crater during the impact. For this, we point out that the liquid, which may be left at the boundaries

of the crater, must be located only in a boundary layer, the thickness of which we may first calculate. Let us calculate, in order of magnitude, the Reynolds number Re for the boundary motion of the liquid:

$$Re = \frac{u \cdot D_p \cdot \rho}{\eta} = \frac{5 \cdot 10^5 \cdot 2}{10^3} = D_p \cdot 10^3 \text{ cm}$$

where D_p is the diameter of the molten part of the crater ("pit") which is related to the diameter of the crater D_s ("zone of crushing") by the relationship $D_p \sim \frac{D_s}{3}$ [31]. For the calculation, we take $\frac{D_s}{D_p} \approx 10$, $\rho \sim 10^3 \text{ g/cm}^3$, and $\eta \approx 10^3 \text{ g/cm}^3$ [32], where η is the viscosity of the liquid, and ρ is the density of the liquid. Then for $D_s > 1 \text{ mm}$, $Re \gg 1$, and the flow will take place with a boundary layer of thickness [33] $\delta_0 \sim \frac{D_p}{\sqrt{Re}} \sim 10^{-3} \sqrt{D_p}$ cm. Hence, even for craters with $D_s = 100 \text{ m}$ and $D_s = 10 \text{ cm}$ (as extreme cases), using the relations given above, we obtain the values $\delta_0 = 1.0 \text{ cm}$ and 0.3 mm , respectively.

It is clear that a layer of thickness 0.3 mm will not flow on the rough ground. Even a layer of thickness $\delta_0 = 1 \text{ cm}$ for a 100-meter crater may, even disregarding its solidification, form puddles at most $\sim 30 \text{ cm}$ deep.

These numbers given an upper limit, since the outer part of the boundary layer will be moving with a high velocity, and, in such an impact, will be thrown from the crater together with the main molten mass. These ejections will take the form of sprays, disintegrating into individual droplets.

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Further, it should be noted that the material thrown out of the crater will possess a maximum stable dimension d_{\max} , such that droplets of larger size do not exist. For this, we use the Rayleigh criterion for stability of sprays [34]:

$$d_{\max} = \frac{\pi^2}{V^2} \cdot \frac{\sigma}{\rho} \quad (40)$$

where V_0 — characteristic velocity of internal movement of the liquid in the drop;

σ — surface tension of the liquid;

ρ — the liquid density.

Taking $V_0 \approx 10^2$ cm/sec, $\sigma = 3 \cdot 10^2$ dynes/cm [32], and $\rho \approx 3$ g/cm³, we find $d_{max} = \frac{10^3}{10^4} \frac{\sigma}{\rho} = 10^{-1}$ cm = 1 mm.

The time constant of solidification in a vacuum is $\tau_s \sim d_{max}$.

A straightforward calculation shows that $\tau_s \approx 2$ sec for $d = 1$ mm, and it is smaller for particles of smaller size [35]. Hence, in such a short time no noticeable volatilization from the drops may take place, since it is possible that, e.g., $\tau_f \sim 10^4 \div 10^3$ sec [41]. An analogous situation exists for still thinner layers of liquid on the surface of the crater. We thus conclude that no noticeable volatilization may take place after impact of a meteor.

Conclusions

1. On the basis of an analysis of laboratory experiments, we have presented a physical model and theory for volatilization of elements in vacuum from molten rock and from the surface of lunar material.

2. The process is one of vaporization of volatile elements from a many-component melt, proceeding in parallel with transformation of the same elements to nonvolatile, tightly bound states (chemical reactions). Such reactions are explained by the interaction of the elements with background gases adsorbed on the surface of the melt. The final, nonzero concentration of volatile elements in the "quasi-stationary" stage is fully explained by the very same mechanism, if all the material was initially in the volatile state.

*Translator's Note: Illegible in foreign text.

3. The temporal evolution of the concentration exhibits three stages: a) slow, b) rapid exponential (kinetic stage), and c) "quasi-stationary" volatilization.

For $p = \sqrt{a_0 z}$ and $T = \sqrt{a_0 z}$ regimes, there clearly appear characteristic parameters P_0 and T_0 determined approximately by the relationship between the speed of volatilization and that for conversion of the elements to nonvolatile states. In the kinetic stage, the temperature dependence of the rate of disappearance of the elements from the melt is determined by the combination of the heats of vaporization L , diffusion A , and adsorption q_v , and the activation energy for oxidation Q . The basis for the individual character of the volatilization of any element from melts of different composition is found in the quantity A .

4. Although in the current work we did not consider in detail /23/ the mechanisms of diffusion of elements to the surface, we may state that always there will be a layer depleted in volatile elements; the thickness of that layer is determined by the relationship between the speeds of volatilization and diffusion. If the volatilization occurs by evaporation from a liquid phase, then the layer will be relatively thick, and if it occurs by sublimation from a solid phase, it will be thin.

5. Laboratory experiments on volatilization of Na and K from molten lunar material have shown [8] that the process proceeds at the beginning in the kinetic stage. This is evidence of the presence of free Na and K in the lunar material. The transition from the kinetic to the "quasi-stationary" stage is understood to be largely an effect of the apparatus. The development of these ideas agrees well with the fact of the general depletion (with respect to Earth) of the lunar surface material in alkali metals, and definitely corroborates the fact that the process of volatilization indeed took place in the oxygen-free atmosphere of the Moon.

6. Calculations show that meteor impacts form liquid in the form of rapidly solidifying particles of small dimensions and thin films. Volatilization under these conditions will be totally insignificant. The basic role in the process of volatilization is played by endogenic processes.

7. The disappearance of various chemically active gases from the lunar atmosphere may have been aided by the chemical binding of these gases adsorbed on the surface during volatilization.

8. Simultaneous comparison of the concentrations of several volatile elements (Na, K, etc.) in lunar rocks of a given type (for example, "sea" basalt) may serve as a supplementary chronological characteristic of different lunar areas. The relationship between concentrations of elements with different volatilities in a given deposit will allow a conclusion about the temperature during the period of formation of that deposit on the Moon.

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9. The key stage of the laboratory modeling for our work was that in which the pressure was varied. The range of pressure we recommend for study of the kinetic stage of volatilization is $p \sim 10^{-3} - 10^{-7}$ torr (with the condition $P_{O_2} \ll p$). For reliable experimental study of P_{O_2} in the lunar atmosphere at the moment of solidification of the surface material, we recommend the range of pressure $p \sim 10^{-12} - 10^{-13}$ torr, although this is obtainable only with great technical difficulties. (We used a pumping speed of $10^5 - 10^7$ l/sec.)

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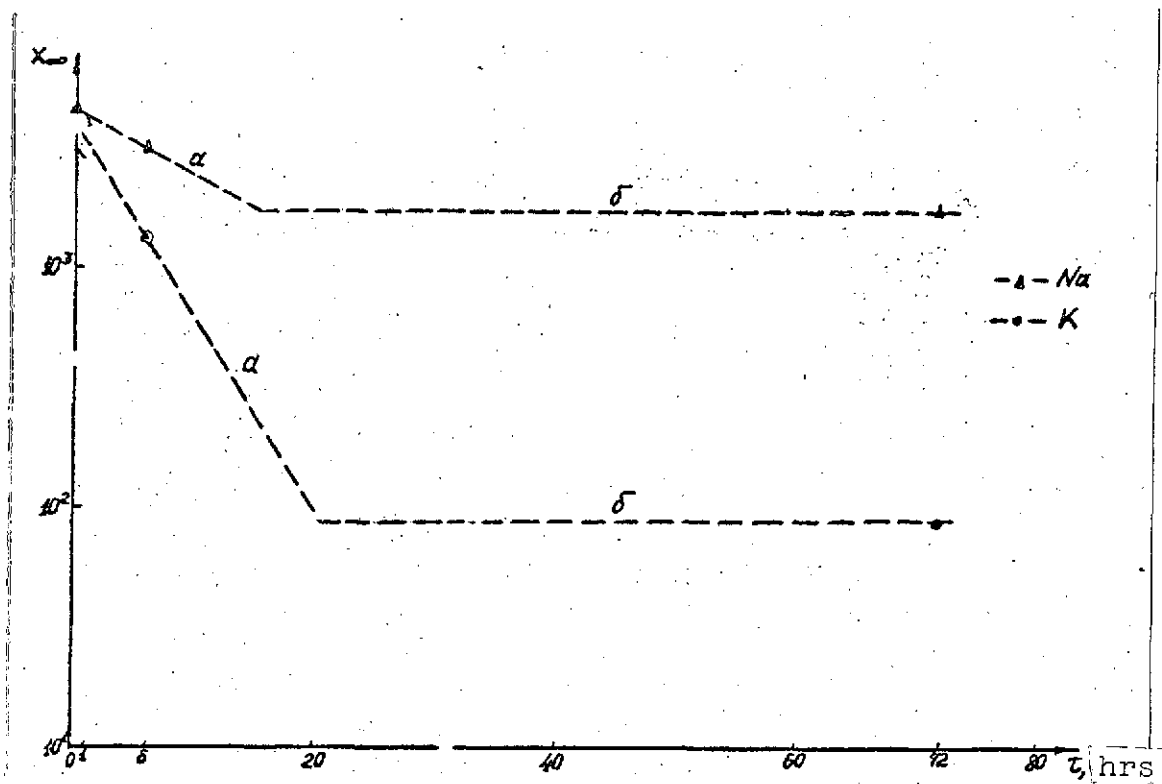


Figure 1. Kinetics of volatilization of Na and K from molten lunar material in vacuum: ($T \approx 1050^\circ\text{C}$; $p \sim 10^{-6}$ torr). [8]

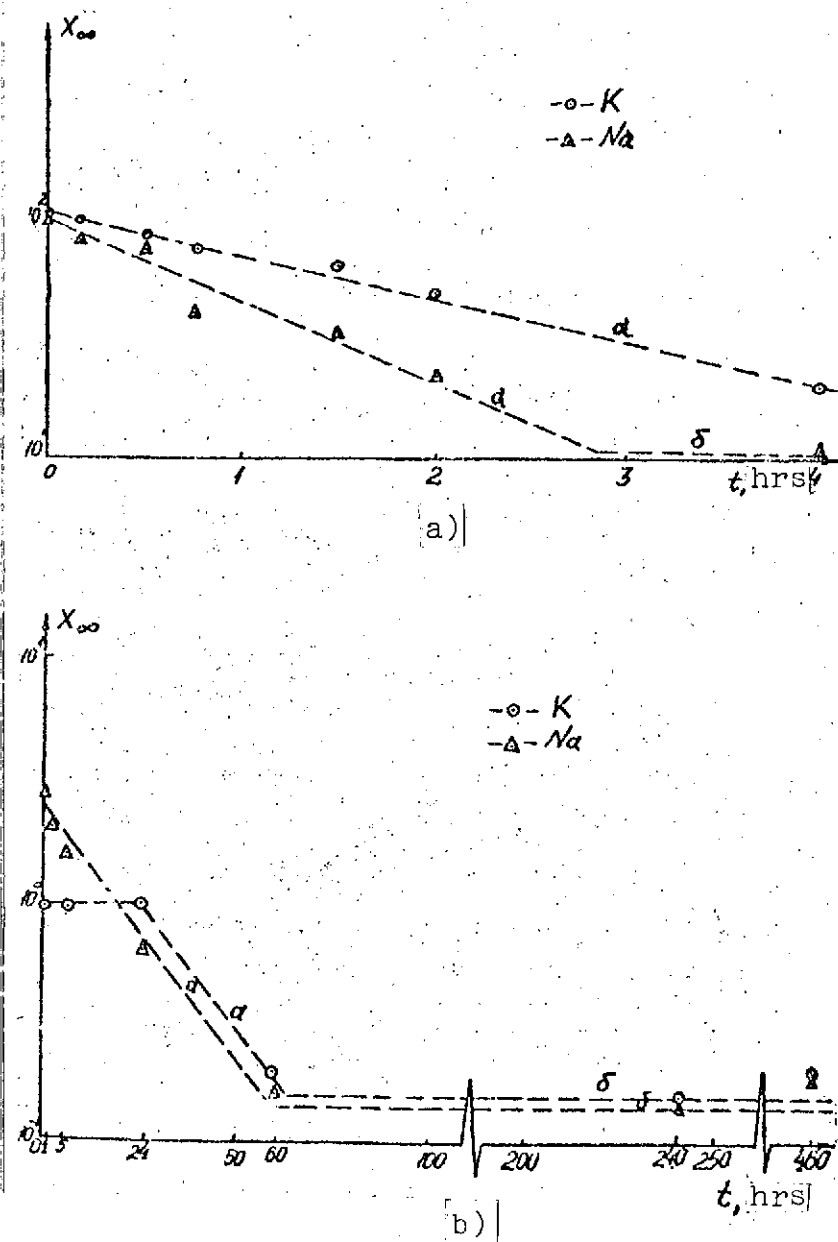


Figure 2. Kinetics of volatilization of Na and K from molten Earth rock in vacuum:
a — $T \sim 1050^{\circ} \text{C}$; $p \sim 10^{-6} \text{ torr}$ [13]; b — $T \sim 1150 - 1175^{\circ} \text{C}$; $p \sim 10^{-4} - 10^{-5} \text{ torr}$ [5, 6]

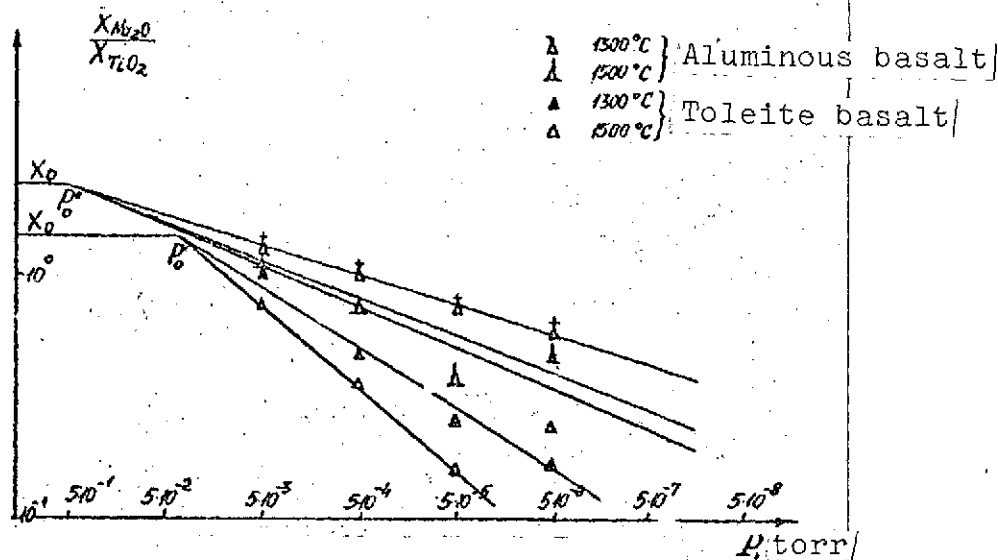


Figure 3. Volatilization of Na in vacuum from aluminous and toleite basalts for $p = \text{var}$ ($T \approx 1300$ and 1500°C) [12]

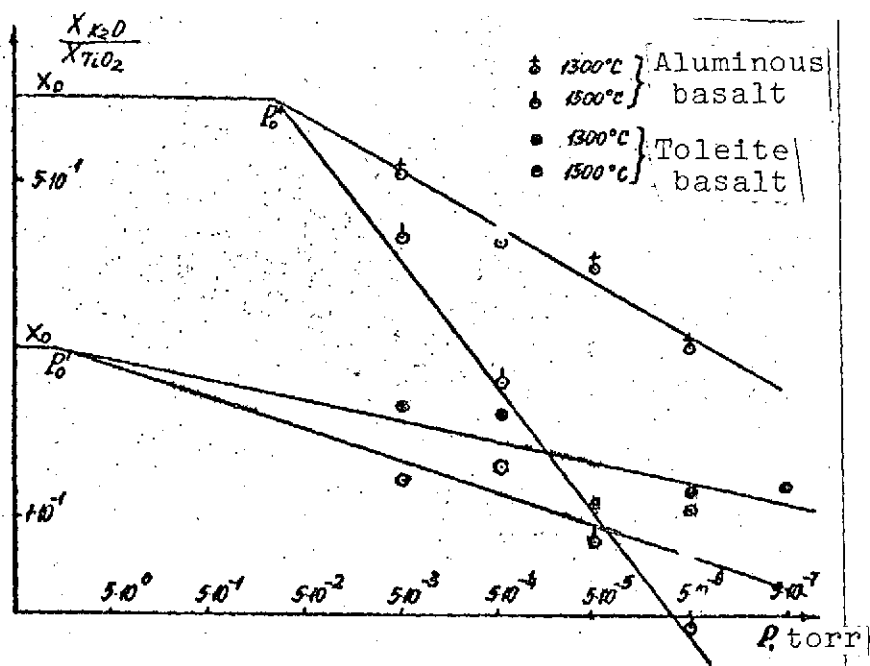


Figure 4. Volatilization of K in vacuum from aluminous and toleite basalts for $p = \text{var}$ ($T \approx 1300$ and 1500°C) [12]

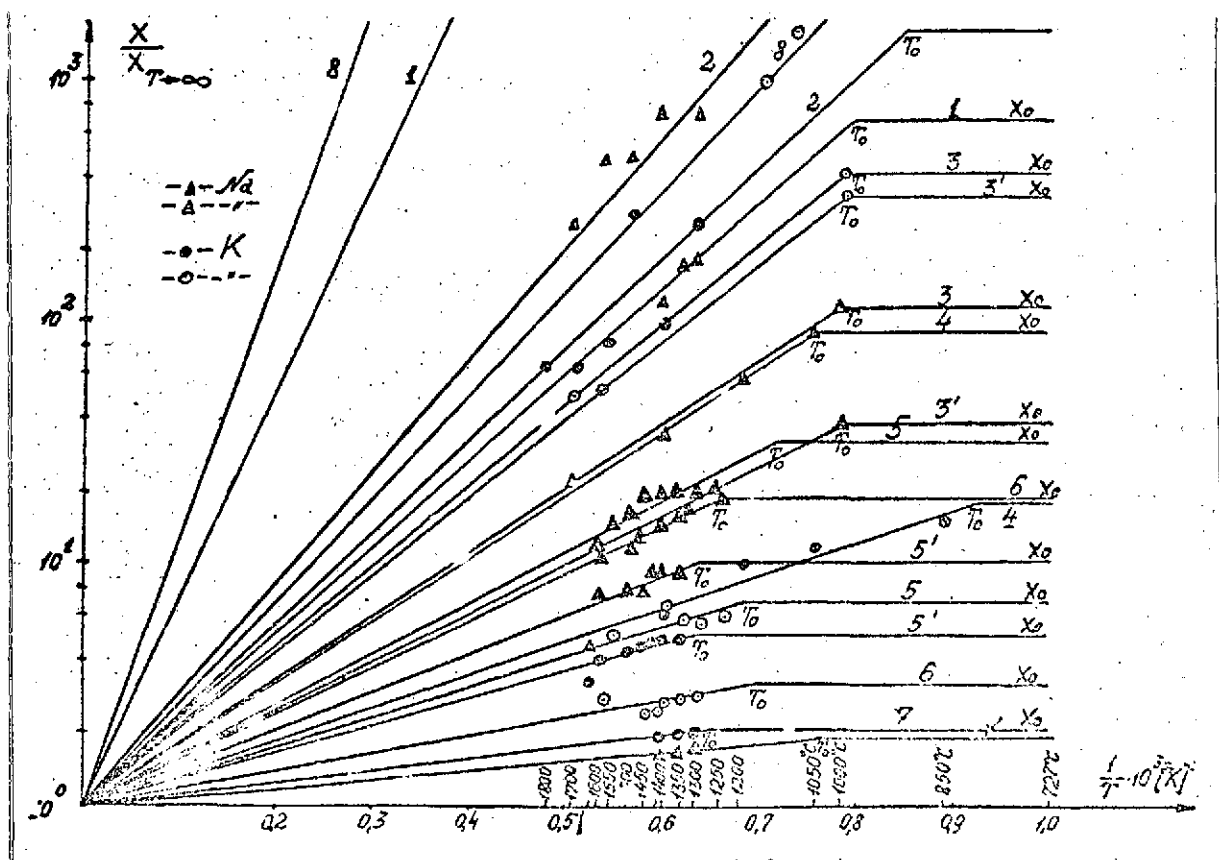


Figure 5. Composite graph [for $T = \text{var of}$ volatilization of Na and K in vacuum ($p \sim 10^{-6}$ torr) from molten Earth rock and minerals (including lunar material)

1 — $\Psi_{\text{Na}} = 7.2$ kcal/mole, $\Psi_{\text{K}} = 17.2$ kcal/mole [11]; 2 — $\Psi_{\text{Na}} = 8.4$ kcal/mole, $\Psi_{\text{K}} = 7.6$ kcal/mole [10]; 3 — $\Psi_{\text{Na}} = 5.3$ kcal/mole; $\Psi_{\text{K}} = 6.6$ kcal/mole [36]; 3' — $\Psi_{\text{Na}} = 4.0$ kcal/mole; $\Psi_{\text{K}} = 6.4$ kcal/mole [36]; 4 — $\Psi_{\text{Na}} = 5.2$ kcal/mole; $\Psi_{\text{K}} = 2.6$ kcal/mole [8]; 5 — $\Psi_{\text{Na}} = 4.2$ kcal/mole, $\Psi_{\text{K}} = 2.4$ kcal/mole [11]; 5' — $\Psi_{\text{Na}} = 3.2$ kcal/mole; $\Psi_{\text{K}} = 2.2$ kcal/mole [11]; 6 — $\Psi_{\text{Na}} = 3.8$ kcal/mole; $\Psi_{\text{K}} = 1.44$ kcal/mole [11]; 7 — $\Psi_{\text{Na}} = 0.74$ kcal/mole; $\Psi_{\text{K}} = 0.94$ kcal/mole [11]; 8 — $\Psi_{\text{Na}} = 22.0$ kcal/mole, $\Psi_{\text{K}} = 8.4$ kcal/mole [13]

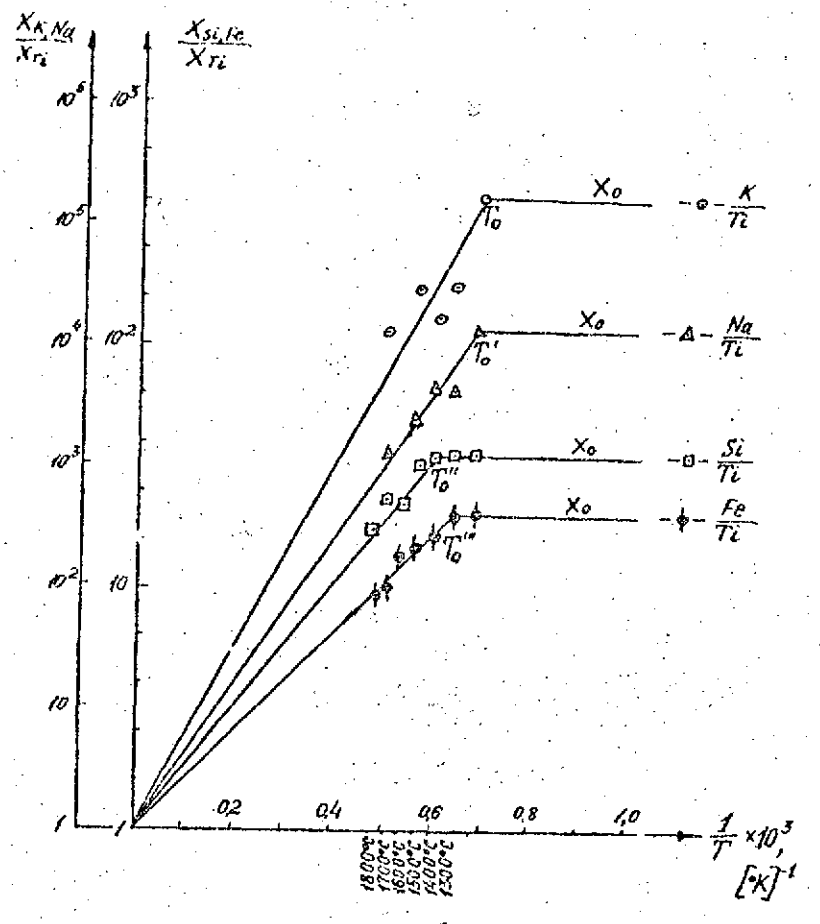


Figure 6. Volatilization of Na, K, Si, and Fe from molten basalt in vacuum ($p \sim 10^{-6}$ torr)

for $T = \text{var}$

$$\psi_K = 31.2 \left| \frac{\text{kcal}}{\text{mole}} \right| \quad \psi_{Na} = 21.6 \left| \frac{\text{kcal}}{\text{mole}} \right| \quad \psi_{Si} = 5.0 \left| \frac{\text{kcal}}{\text{mole}} \right| \quad \psi_{Fe} = 5.4 \left| \frac{\text{kcal}}{\text{mole}} \right|$$

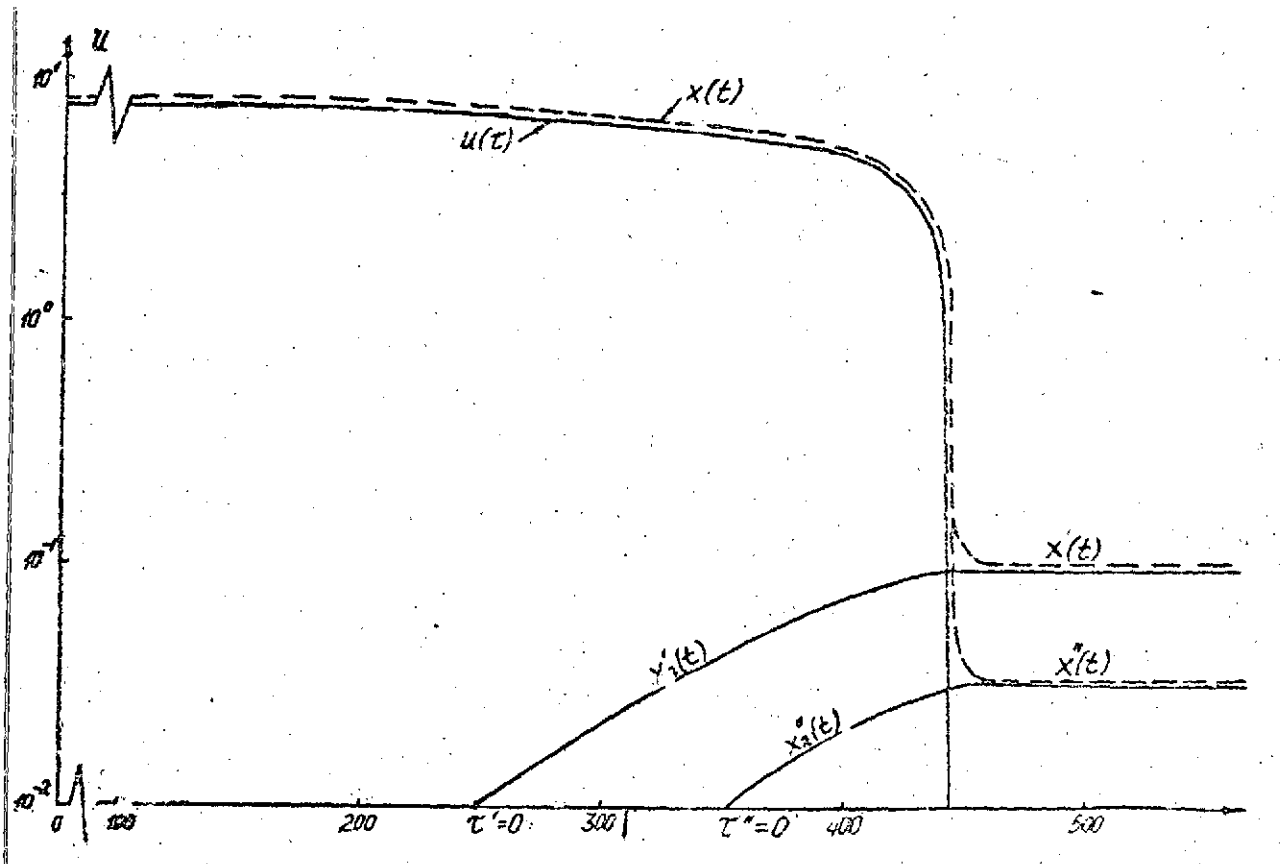


Figure 7. The universal function $u(t)$, and also the functions $x(t)$ and $x'_2(t)$, and $x''_2(t)$

REFERENCES

1. Vinogradov, A. P. *Geochim. Cosmochim. Acta*, Suppl., Vol. 2, No. 1, 1971, p. 16. /25
2. O'Hara, M. J. *Nature*, Nov. 10, 1972, p. 240.
3. Naughton, J. J., I. L. Barnes and D. A. Hammond. *Science*, Vol. 149, No. 3684, 1965.
4. Vonneguth, B., R. K. McConnell and R. V. Allen. *Nature*, Vol. 20, No. 5022, 1966.
5. Gutkin, A. M., Ts. M. Raytburd et al. "Trudy Geologicheskogo Instituta AN SSSR", Vol. 204, 1969.
6. O'Hara, M. J., G. M. Biggar and S. W. Richardson. *Science*, Vol. 167, 1970, p. 607.
7. O'Hara, M. J., G. M. Biggar, S. W. Richardson, C. E. Ford and B. G. Jamieson. *Geochim. Cosmochim. Acta*, Suppl., Vol. 1, No. 1, 1971, p. 704.
8. Gibson, E. K., Jr. and N. J. Hubbard. *Geochim. Cosmochim. Acta*, Suppl., Vol. 2, No. 3, 1972, p. 2003.
9. Nusinov, M. D., V. A. Kochnyev, Yu. B. Chernyak et al. In the Collection: "Sovremenniy predstavleniya o Lune" [Modern Concepts About the Moon]. Nauka Press, 1972.
10. Yakovlev, O. I., A. I. Kosolapov, A. V. Kuznetsov and M. D. Nusinov. *DAN SSSR*, Vol. 206, No. 4, 1972.
11. Yakovlev, O. I., A. I. Kosolapov, A. V. Kuznetsov and M. D. Nusinov. *Vestnik MGU, Seriya Geologicheskaya*, No. 5, 6, 1973.
12. Yakovlev, O. I. Dissertation, presented in competition for the scholarly degree of Master of Geologic-Mineralogic Science, MGU, Moscow, 1974.
13. Storey, W. Ch. *Nature, Ph. Sci.*, Vol. 241, Feb. 26, 1973.
14. Walter, L. S. and R. T. Dodd. *Meteoritics*, Vol. 7, No. 3, Sept. 30, 1972; *Solar Energy*, Vol. II, No. 3-4, July-December, 1967.
15. Taylor, S. R. *Nature*, Vol. 245, Sept. 28, 1973. /26
16. Knudsen, M. *Ann. Phys.*, Vol. 47, 1915, p. 697.
17. Khirs, D. and G. Pound. *Ispareniye i kondensatsiya (Evaporation and Condensation)*. Metallurgizdat, 1966.

18. Pol, V. Raketnaya Tekhnika (Russian translation), No. 9, September, 1962.
19. Geyntse, V. Vvedeniye v vakuumnyuyu tekhniku (Introduction to Vacuum Technology). "Gosenergoizdat", Moscow-Leningrad, 1960.
20. Shampe, R. Fizika i tekhnika electrovakuumnikh priborov (Physics and Technology of Elektro-vacuum Apparatus). "Gosenergoizdat", Moscow-Leningrad, 1963.
21. Hildebrand, J. H. and R. L. Scott. The Solubility of Non-Electrolytes. Third Edition. N. Y., 1950.
22. Kozlov, L. V., M. D. Nusinov et al. Modelirovaniye teplovikh rezhimov kosmicheskovo apparata u okruzhayushchey yevo sredi (Modeling of the Thermal Modes of Spacecraft and Their Surrounding Environment). "Mashinostroyeniye", Moscow, 1971.
23. Nusinov, M. D., B. N. Pyak and Yu. B. Tchernyak On the Choice of Criteria for Laboratory Simulation of Space Vacuum Effects on Spacecraft System Elements. Preprint, Institute for Space Research, Academy of Sciences of the USSR, Moscow, 1973.
24. Kubo, R. Termodinamika (Thermodynamics). [Mir] Press, Moscow, 1970.
25. Filder, B. (ed.) Geology and Physics of the Moon. Elsevier Pub. Co., Amsterdam - London - N. Y., 1971.
26. Yanke, Ye., F. Emde and F. Leish. Spetsial'niye funtsii (Special Functions). Nauka Press, Moscow, 1968.
27. Landau, L. D., A. I. Akhizer and Ye. M. Lifshitz. Mekhanika i molekulyarnaya fizika (Mechanics and Molecular Physics). Nauka Press, Moscow, 1969.
28. Frenkel', Ya. Kineticheskaya teoriya zhidkosti, sobraniye izbrannikh trudov (Kinetic Theory of Liquids, Collection of Published Works), Vol. III. Academy of Sciences USSR, Moscow-Leningrad, 1959.
29. Blander, M., K. Keil, L. S. Nelson and S. R. Skaggs. Science, Vol. 170, No. 3956, Oct. 23, 1970. /27
30. Zel'dovich, Ya. B. and Yu. P. Rayzer. Fizika udarnikh voln i vysokotemperaturnykh gidrodinamicheskikh yavleniy (The Physics of Shock Waves and High Temperature Hydrodynamic Phenomena). Nauka Press, 1966.

31. Herz, F., D. Hartung and D. Gault. Earth and Planetary Science Letters, Vol. 10, 1971, pp. 381-386.
32. Pugh, M. J. Nature, No. 11223, 1972.
33. Schlichting, G. Teoriya pogranichnovo sloya (Boundary Layer Theory). IL Press, 1956.
34. Strett, C. (Lord Rayleigh). Teoriya zvuka (Theory of Sound), Vol. II, OGIZ GITTL, Moscow-Leningrad, 1944.
35. O'Keefe, J. A. J. Geoph. Res., Vol. 76, 1971, p. 26.

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